Supplementary Materials:

Bis(triphenylphosphine)iminium Salts of Dioxothiadiazole Radical Anions: Preparation, Crystal Structures, and Magnetic Properties

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contacts between them. The asymmetric unit contains one green and one blue molecule. The most efficient π-π orbitals overlap is between light blue and navy blue molecules.

Table S1. Details of single crystal X-Ray data and structural refinement for **PPN(L)**, **PPN(BrL)**, **PPN(4,7-L) PPN(diBrL), diBrL and BrL.**

		PPN(4,7-L)	**PPN(BrL)**	**PPN(L)**	**BrL**	**diBrL**	**PPN(diBrL)***
CCDC deposition number		1882328	1882331	1882329	1882326	1882327	1882330
formula		$C_{48}H_{36}N_5P_2O_2S$	$C_{54}H_{30}N_5P_2BrO_{3.5}$	$C_{54}H_{49}N_5P_2O_{5.25}S$	$C_{12}H_5BrN_4O_2S$	$C_{12}H_4Br_2N_4O_2S$	$C_{48}H_{34}Br_2N_5O_2P_2S$
FW [g·mol^{-1}]		808.82	978.74	929.98	349.17	428.07	966.62
T [K]		120(1)	120(1)	120(1)	120(1)	120(1)	117(2)
wavelength (radiation)		0.71073 Å (Mo Kα)	0.71073 Å (Mo Kα)	0.71073 Å (Mo Kα)	0.71073 Å (Mo Kα)	0.71073 Å (Mo Kα)	0.71073 Å (Mo Kα)
space group		*P*2$_1$/*c*	P-1	P-1	P-1	*P*2$_1$/*c*	*P -1*
unit cell	*a* [Å]	9.4226 (3)	11.525 (3)	11.451 (8)	5.0133 (8)	6.7679 (9)	14.3233(6)
	b [Å]	16.9415 (4)	14.122 (4)	14.378 (8)	11.1415 (19)	8.6646 (13)	15.7838(7)
	c [Å]	26.2571 (7)	16.056 (4)	15.701 (12)	11.3099 (18)	22.801 (3)	21.0047(9)
	α (°)	90.0	70.664 (8)	112.01 (3)	69.183 (4)	90.0	92.144(2)
	β (°)	98.046 (2)	75.272 (9)	102.19 (4)	87.853 (4)	96.888 (4)	91.480(2)
	γ (°)	90.0	89.129 (10)	90.15 (3)	85.141 (4)	90.0	116.651(2)
V [Å^3]		3997.9 (1)	2377.8 (11)	2333 (3)	588.34 (17)	1327.4 (3)	4236.3(3)
Z		4	2	2	2	4	4
density [g·cm^{-3}]		1.376	1.367	1.324	1.971	2.142	1.516
abs. coeff. *μ* [mm^{-1}]		0.214	1.03	0.19	3.68	6.27	2.086
crystal description		Deep-Purple Block	Deep-Purple Plate	Deep-Purple plate	Yellow Needle	Orange Needle	Deep-Purple Plate
crystal size [mm^3]		0.14 × 0.14 × 0.1	0.39 × 0.26 × 0.04	0.37 × 0.33 × 0.1	0.18 × 0.06 × 0.03	0.14 × 0.04 × 0.01	0.09 x 0.08 x 0.02
F(000)		1684	996	976	344	824	1956
collection *θ* range [deg]		3.362 – 25.048	3.1 – 27.9	2.7 – 27.5	3.2 – 24.9	2.5 – 26.5	2.4 – 26.45
collected reflections		29322	24850	18355	2847	8552	24318
independent reflections		6728	11119	10293	1996	2713	18276
R_{int}		0.0447	0.075	0.021	0.035	0.085	twin
completeness [%]		97.3	98.1	97.4	98.1	98.7	99.8
refinement method		Full-matrix least-squares on F^2					
data/restraints/parameters		6728/0/523	11119/5/563	10293/21/608	1996/0/181	2713/48/190	24318/0/1082
GOF on F^2		1.015	1.029	1.058	1.012	1.022	1.07
R_1 [$I > 2\sigma(I)$]**		R_1 = 0.0401	R_1 = 0.068	R_1 = 0.061	R_1 = 0.044	R_1 = 0.048	R_1 = 0.0555
wR_2 [all data]		wR_2 = 0.0936	wR_2 = 0.195	wR_2 = 0.163	wR_2 = 0.109	wR_2 = 0.089	wR_2 = 0.1337
Max./min. residual density [e·A^{-3}]		0.292 −0.423	1.06 −1.03	0.68 −0.63	0.78 −0.61	0.82 −0.87	0.783 -0.966

* Refined as a two component twin with scales: 0.6227(6) and 0.3773(6)

** $R_1 = \Sigma[|F_0|-|F_c|]/\Sigma|F_0|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2F_0^2 + (0.0323P)^2 + 18.2463P]$; $P = (F_0^2 + 2F_c^2)/3$

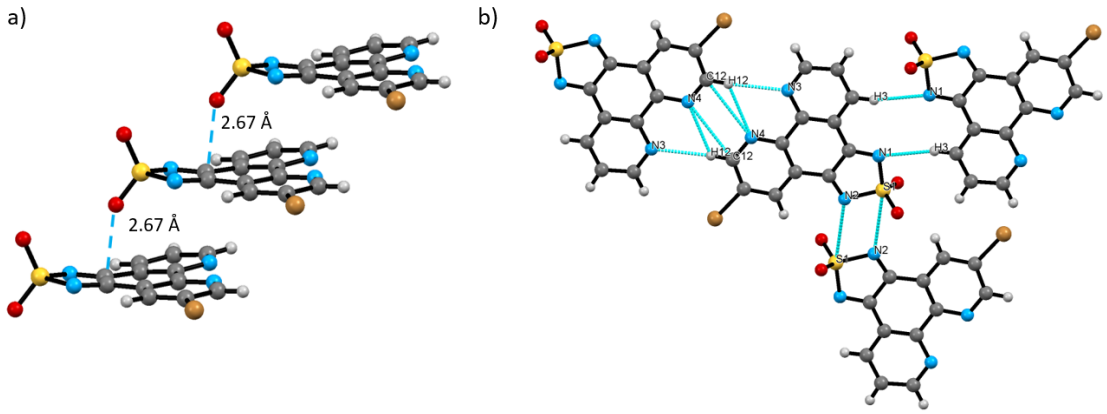

Figure S1. Illustration of molecular stacks in **BrL** with marked short σ-π contacts a) and fragment of a supramolecular layer with marked contacts that are shorter than the sum of the Van der Waals radii b) (made using Mercury program).

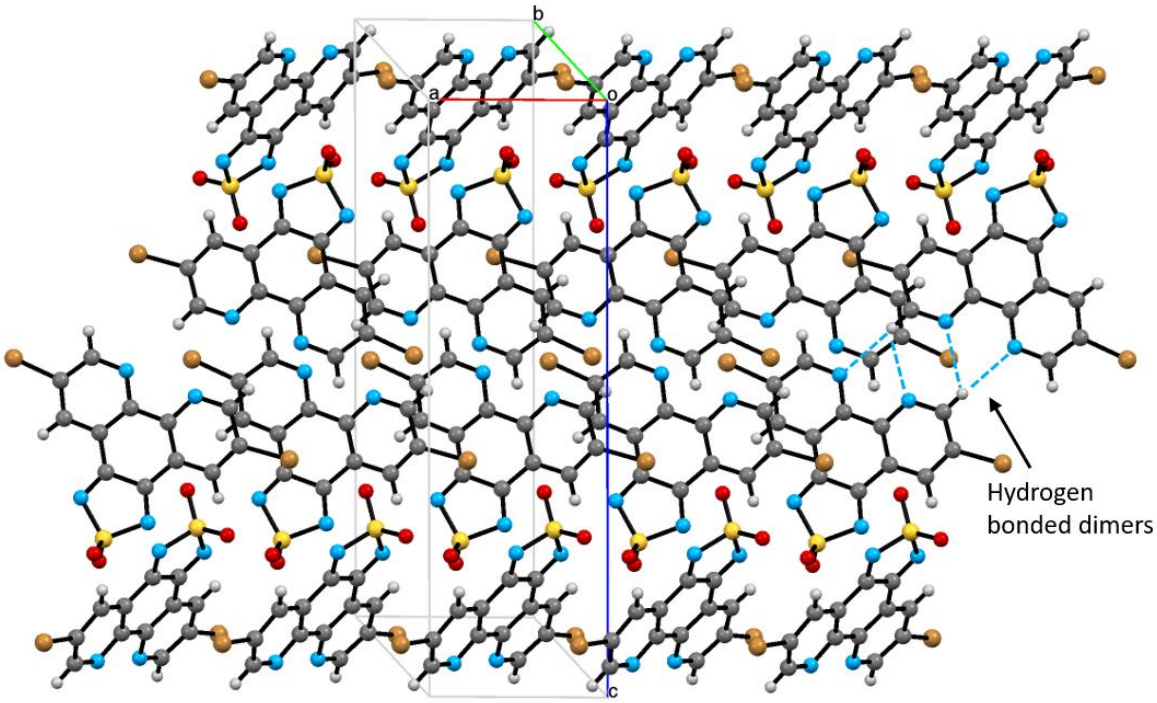

Figure S2. Illustration of crystal packing of **diBrL**. The supramolecular chains of parallel hydrogen bonded dimers run through the structure interacting via π-orbitals and short contacts with Bromine atoms.

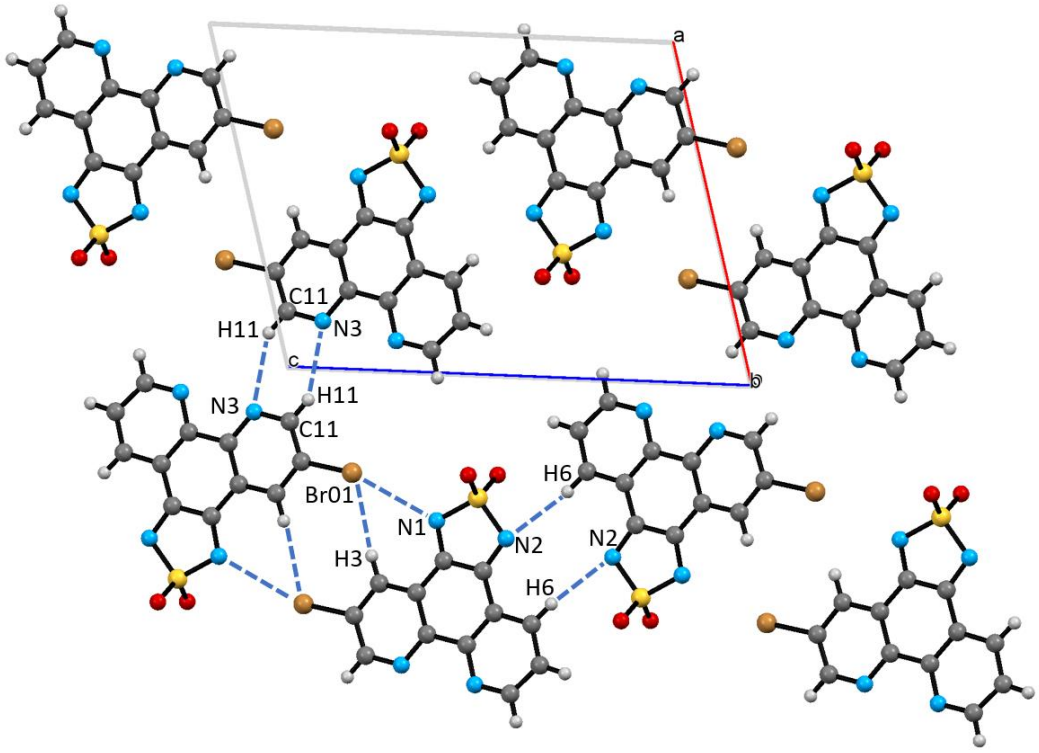

Figure S3. Illustration of **PPN(BrL)** supramolecular layers. Contacts between BrL anions that are shorter than the sum of the Van der Waals radii.

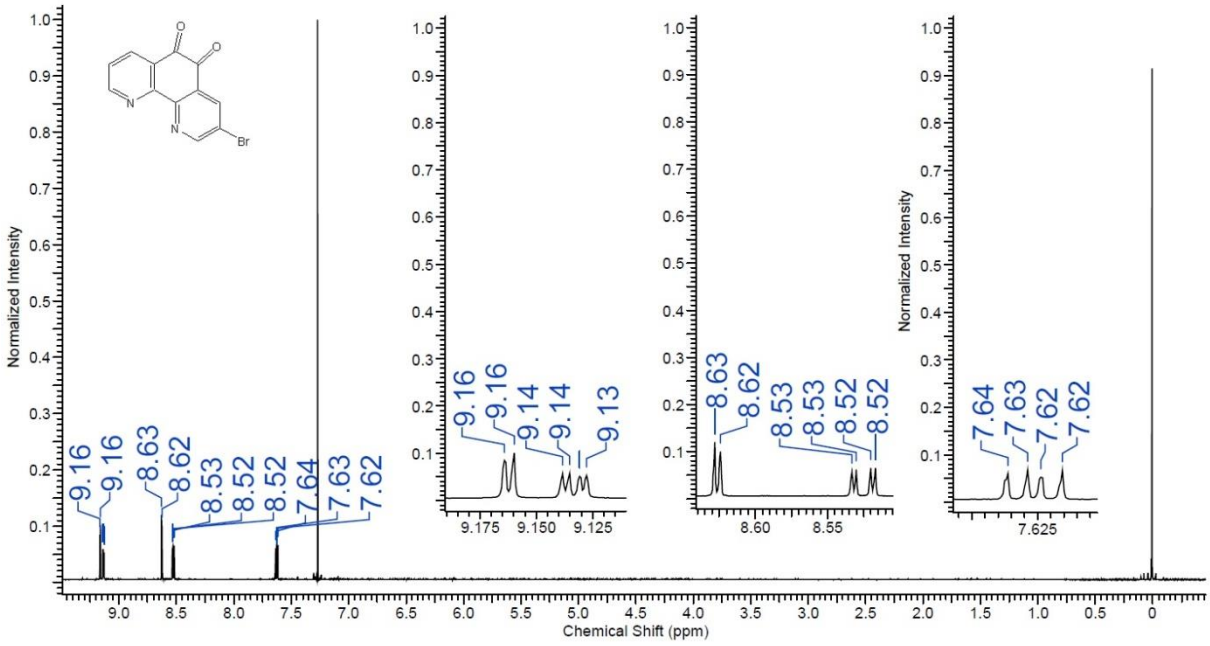

Figure S4. NMR spectrum of 3-bromo-1,10-phenantroline-5,6-dione.

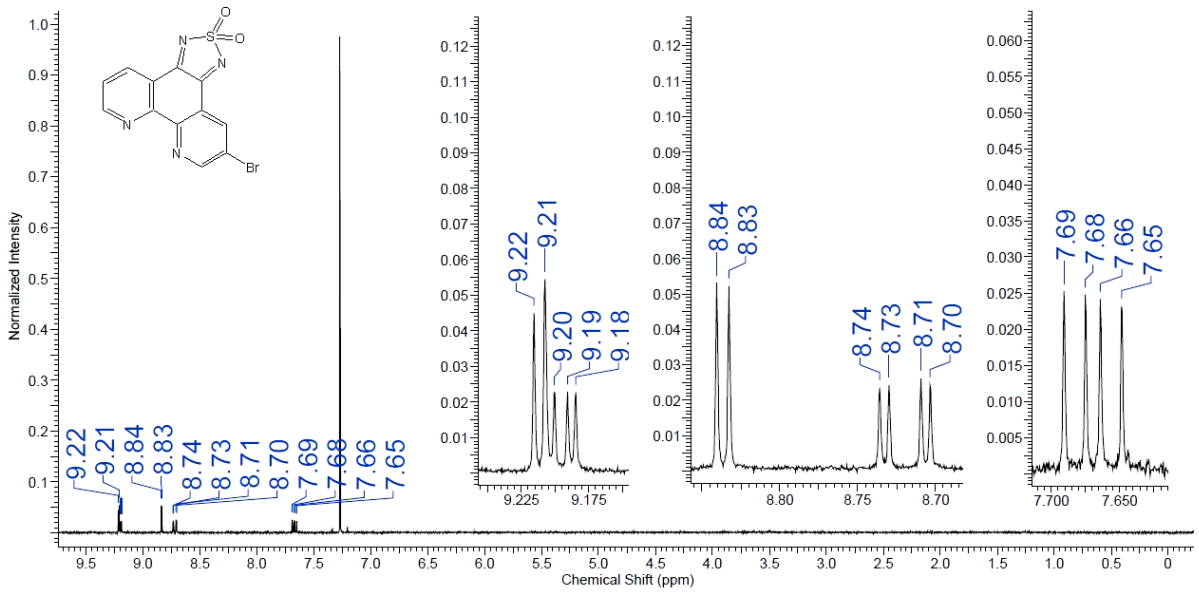

Figure S5. NMR spectrum of 5-bromo-[1,2,5]thiadiazolo[3,4-f][1,10]phenanthroline 2,2-dioxide **BrL**.

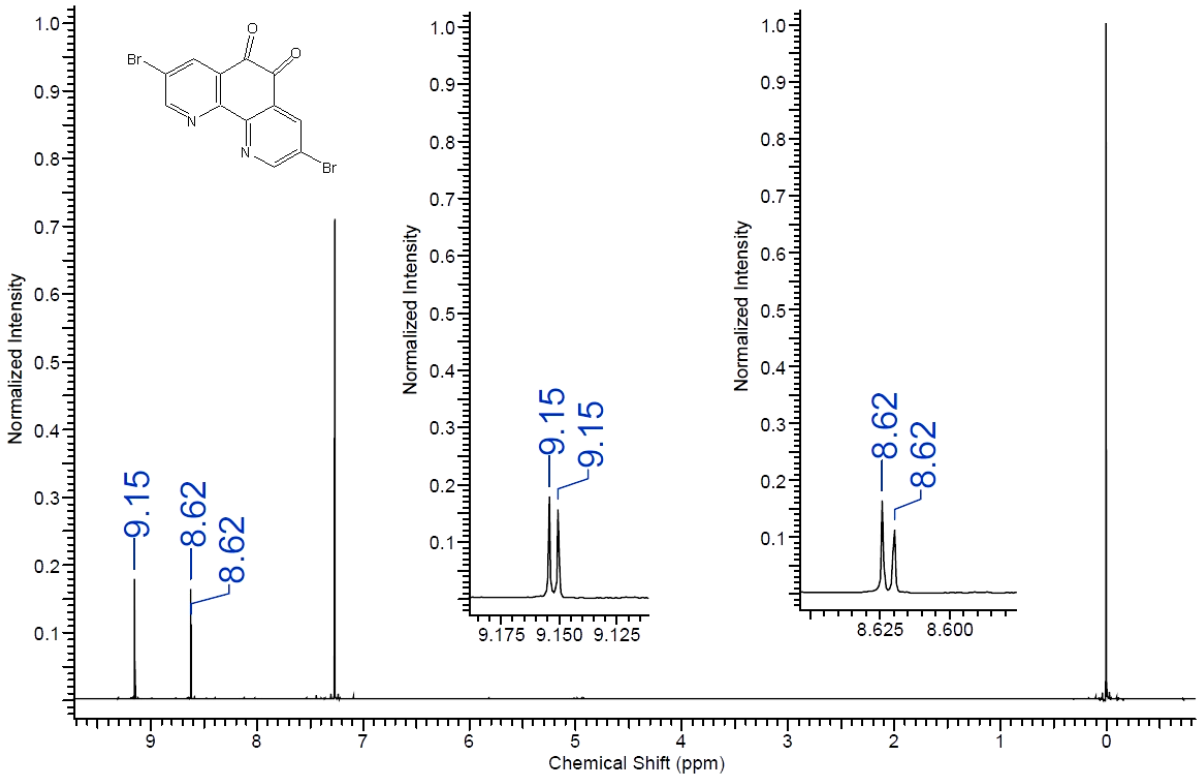

Figure S6. NMR spectrum of 3,8-dibromo-1,10-phenantroline-5,6-dione.

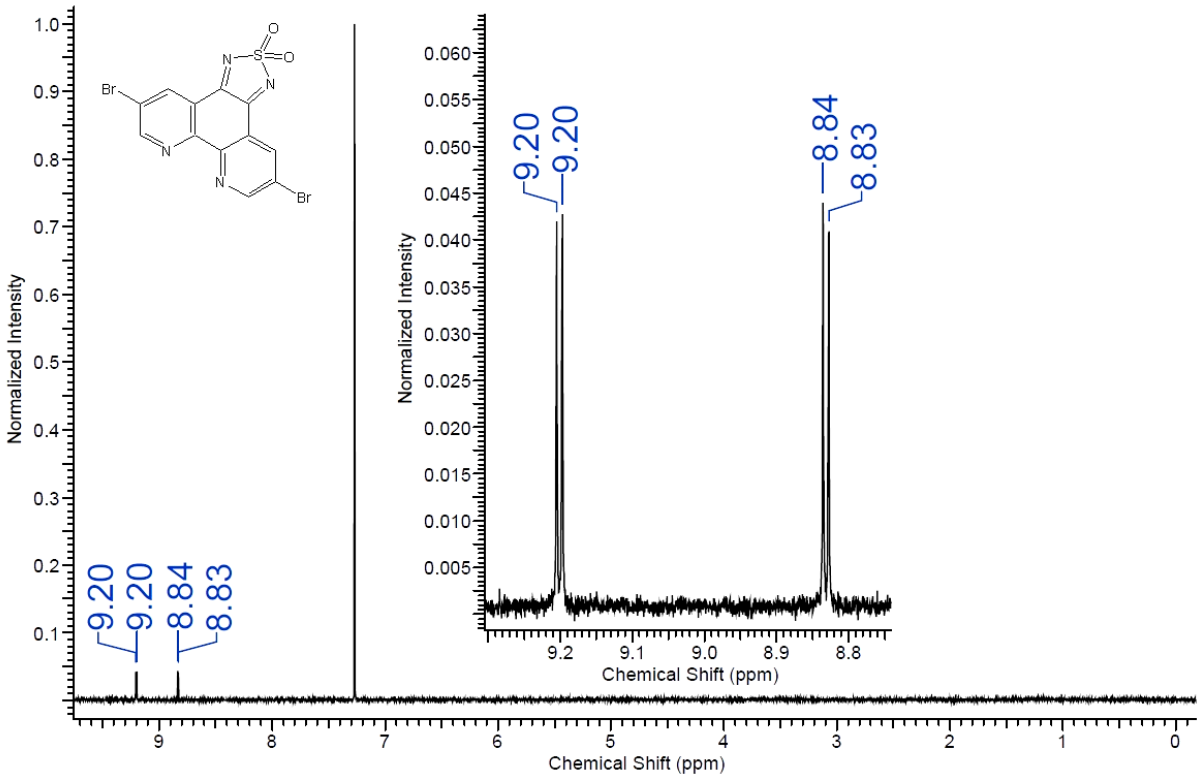

Figure S7. NMR spectrum of 5,10-dibromo-[1,2,5]thiadiazolo[3,4-f][1,10]phenanthroline 2,2-dioxide **diBrL**.

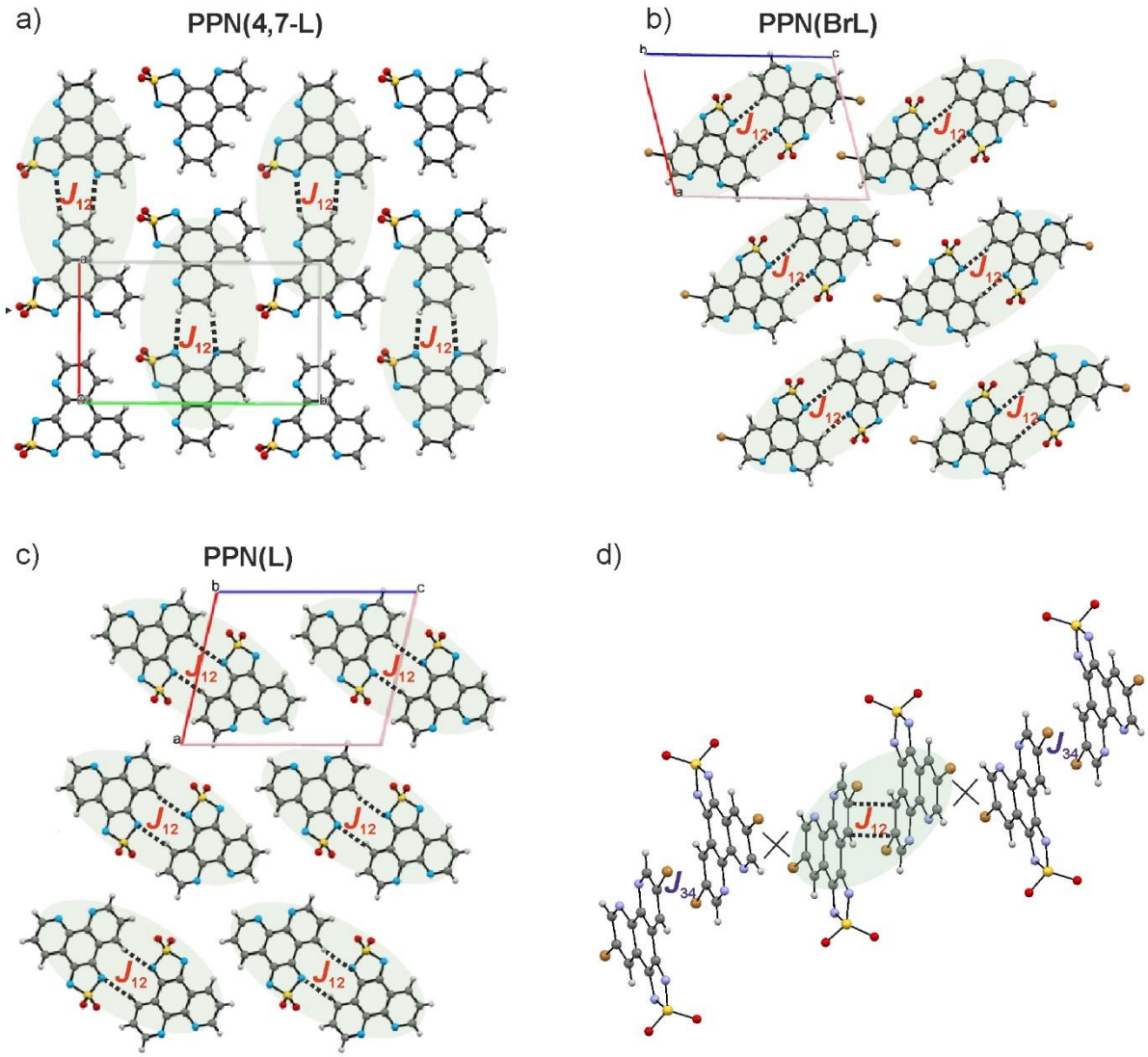

Figure S8. Superexchange coupling scheme in **PPN(4,7-L)** (a), **PPN(BrL)** (b), **PPN(L)** (c) and **PPN(diBrL)** (d). The green ovals and dotted lines indicate the magnetic interaction pathways taken into account in the fitting of the magnetic data. In the case of **PPN(diBrL)** (d) two interaction pathways are considered: J_{12} and J_{34} with the assumption that $J_{12} >> J_{34}$.

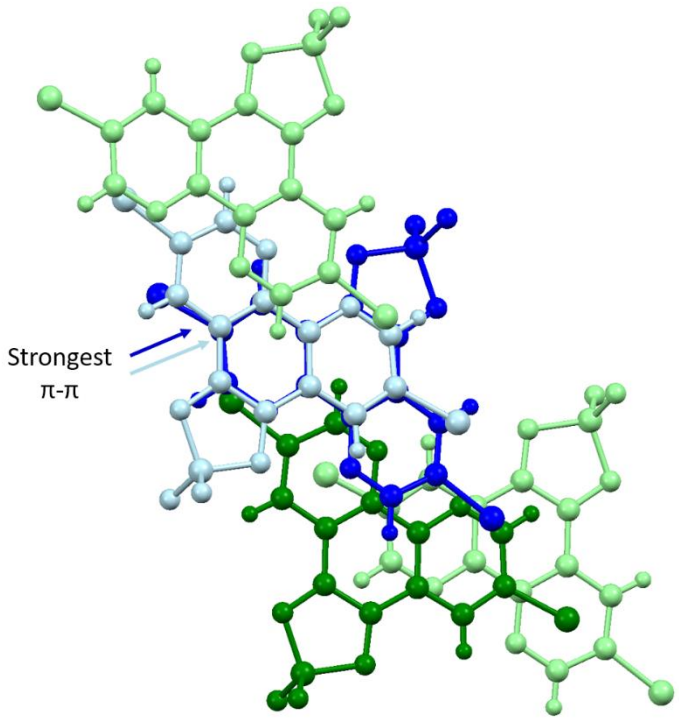

Figure S9. Illustration of supramolecular stack of diBrL anions in the crystal structure of **PPN(diBrL)**. The molecules are color coded to depict different intermolecular contacts between them. The asymmetric unit contains one green and one blue molecule. The most efficient π-π orbitals overlap is between light blue and navy blue molecules.